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HYDROLYZED POLYACRYLONITRILE POLYMERS AND PROCESS OF PREPARING SAME

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The present invention relates to novel polymeric derivatives, particularly novel derivatives of polyacrylonitriles, and to processes of producing such derivatives.

It is one object of this invention to provide novel polymers, particularly novel polymers which are derived from polyacrylonitrile.

It is a further object of this invention to provide novel polymers which are soluble in aqueous solutions under acidic conditions.

It is a further object of this invention to provide a process for preparing novel polymeric derivatives from polyacrylonitrile, particularly polymeric derivatives which are soluble in aqueous solutions under acidic conditions.

Still further objects and advantages of this invention will become apparent from the following description and the appended claims.

The novel polymers of this invention comprise essentially a polyacrylonitrile in which from 40 to 80% of the nitrile groups have been hydrolyzed to carboxyl groups. The polymers may contain minor amounts of chemically combined modifying agents such as styrene, vinyl acetate, alkyl methacrylates, alkyl acrylates, acrylic acid or methacrylic acid as will be pointed out in greater detail hereinafter.

The novel polymers of this invention are prepared in general by first hydrolyzing a suspension or a substantially stable aqueous dispersion or emulsion of a polyacrylonitrile with an alkaline hydrolyzing agent, preferably an alkali metal hydroxide, while maintaining the polymer in a dispersed or emulsified state, until at least 40% of the nitrile groups of the polymer have been hydrolyzed to

$$-\overset{\overset{\large O}{\|}}{C}-O-X$$

groups, where X is the cation of the hydrolyzing agent, and then precipitating the hydrolyzed polymer from the aqueous medium by means of an acid, preferably in the form of a plastic, coherent mass, whereby the

$$-\overset{\overset{\large O}{\|}}{C}-O-X$$

groups in the hydrolyzed polymer are converted to carboxyl groups. The precipitated polymer is preferably extracted to remove a substantial portion of electrolytes and acid anions therefrom and thereafter it is dried or is dissolved in an aqueous medium.

The aqueous suspension, dispersion or emulsion of the polymer used in the processes of this invention may be prepared in various ways. One suitable procedure comprises heating, preferably at the reflux temperature, an aqueous emulsion of monomeric acrylonitrile in the presence of a polymerization catalyst and an amount of an emulsifying agent sufficient to provide a suspension or stable dispersion or emulsion during and after polymerization. This procedure is conventional and is well known in the art. The emulsion polymerization procedure may be modified to provide low molecular weight polymers

by the use of relatively large amounts of organic peroxide or by the use of retarders such as beta nitro styrene or the retarders disclosed generally in United States Patent No. 2,537,015. Chain transfer agents may also be used.

The polymers produced by the foregoing procedure may be modified to some extent by incorporating a vinyl monomer, which is copolymerizable with acrylonitrile and contains a single $CH_2{=}C<$ group. As examples of such vinyl monomers may be mentioned styrene or ring substituted styrene, vinyl acetate, alkyl methacrylates such as methyl methacrylates, alkyl acrylates such as methyl acrylate and the like. The amount of modifying monomer used depends primarily on the particular monomer employed. In the case of styrene or ring substituted styrene amounts up to 10% by weight, based on the total monomers, may be used while in the case of alkyl methacrylates amounts up to 20% by weight, based on the total monomers, may be employed. In those instances where vinyl acetate or alkyl acrylates, or both, are used as modifying monomers, it is possible to use up to 45% of such monomers, based on the total monomers. When modifying vinyl monomers are used as described above and the rate of reaction between the modifying monomer and the acrylonitrile is not the same as the homopolymerization rate of the acrylonitrile, it is usually necessary to add the modifying monomer and the acrylonitrile to an aqueous solution of a polymerization catalyst and emulsifying agent, while heating, at substantially the same rate as the reaction rate of such modifying monomer and the acrylonitrile in order to obtain the final polymer (which is really a copolymer) of uniform composition. The use of modifying monomers as described above introduces various complications in the polymerization procedure and also alters, somewhat, the properties of the polymers of this invention. However, the use of modifying monomers does have the advantage of enabling the preparation of stable dispersions which are easier to saponify and hydrolyze than suspensions of relatively coarse particles of homopolymers of acrylonitrile. For this reason it is preferred to employ such modifying monomers.

By using up to 3%, preferably 1 to 2%, by weight of the total monomers of acrylic acid, methacrylic acid or, in some cases, alkyl acid esters of maleic acid, with the acrylonitrile or with the acrylonitrile and modifying monomers hereinbefore described it is possible to produce aqueous polymeric dispersions or emulsions which have greater stability during the subsequent hydrolysis step, even without the addition of added emulsifying agents, and accordingly the use of such modifying monomers is preferred in the preparation of the starting dispersions or emulsions employed in the processes of this invention.

In carrying out the emulsion polymerization procedure described above, it is possible to use a wide variety of emulsifying or dispersing agents, including anionic surface active agents which are soluble under acid conditions, for example, alkali metal salts of alkyl benzene sulfonic acids, in which the alkyl group contains 10 or more carbon atoms, sulfated alcohols containing 10 or more carbon atoms and alkali metal salts of sulfo dialkyl succinic acid, and non-ionic sulface active agents such as polyoxyethylene esters of tall oil or alkylated phenols, in which the alkyl group contains at least 8 carbon atoms. Other emulsifying agents conventionally used in acidic emulsion polymerization processes will be apparent to those skilled in the art. A wire variety of emulsion polymerization catalysts may be used including potassium persulfate and the organic peroxides such as benzoyl peroxide and the like.

Stable aqueous dispersions of polyacrylonitirile per se or the modified polyacrylonitrile may be prepared by